Transition-state Structure in Thermal β-*cis*-Elimination of Esters

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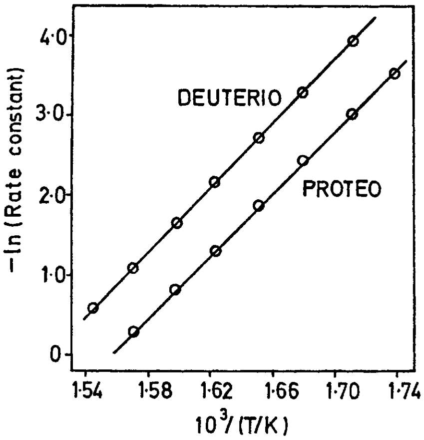
Summary A maximum kinetic deuterium isotope effect, corresponding to ΔE_a, the difference in zero point C–D and C–H vibrational energies and $\Delta(\Delta S^{\ddagger}) = 0$, determined for both t-butyl and ethyl ester thermolysis, is interpreted as evidence supporting only a symmetrical, non-heterolytic, transition state which is non-planar and analogous to that of other pericyclic fragmentations.



Figure

A recent article[1] presents a generalized description of the *β-cis* thermolytic ester elimination reaction transition state, comparing it to the solvolytic analogue which encompasses a spectrum of possible structures ranging from carbonium to carbanion-like extremes. While this concept is attractive, it may not correlate in many respects with data we have also reported[2] recently on the thermolysis of analogous carbamates. Thus, the absence of randomization of an ^{18}O label in the unchanged substrate, when the more readily (than carboxylic ester) decomposable t-butyl carbamate ester undergoes partial gas-phase thermolysis, indicates that any ion pairing characteristic of the thermolysis transition state could not have persisted for as much as one free rotation.

Table

Activation parameters in thermolysis of esters

Substrate	Temp. range	E_a/(kcal mol^{-1})	$\Delta S^{\ddagger}_{330}$/(cal K^{-1} mol^{-1})	log *A*
t-Butyl *NN*-dimethylcarbamate	302—363°	39·0 ± 0·1	−1·2 ± 0·2	13·27 ± 0·03
[$^2H_9$]-t-Butyl *NN*-dimethylcarbamate	311—374°	40·3 ± 0·1	−0·8 ± 0·2	13·37 ± 0·05

$\Delta E_a = 1{\cdot}30 \pm 0{\cdot}15$ kcal/mol; theor. $\Delta E_a = 1{\cdot}15$ kcal/mol. $\Delta(\Delta S^{\ddagger}) = 0{\cdot}4 \pm 0{\cdot}4$ cal K^{-1} mol^{-1}; theor. $\Delta(\Delta S^{\ddagger}) = 0$ cal K^{-1} mol^{-1}

Compare results of Blades and Gilderson[5] on thermolysis of ethyl acetate: $k_H = 3{\cdot}86 \times 10^{-12} \exp(-48{,}000 \pm 400)$; $k_D = 4{\cdot}84 \times 10^{-12} \exp(-49{,}500 \pm 300)$.

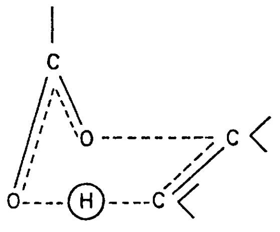
The rates of ethyl, isopropyl, and t-butyl carbamate ester thermolysis have also been compared recently[3]. These authors have also urged that the activation parameters observed are indicative of an unsymmetrical transition state of thermolysis involving heterolytic fission of the critical bonds.

It has been experimentally demonstrated[4] that a fully symmetrical transition state is characterized by a maximum kinetic deuterium isotope effect. The 'maximum' k_H/k_D value, corresponding to the zero point energy difference in C–H and C–D stretching vibrations would be associated only with the coaxial geometry (or nearly so) of an O · · ·H · · · C array in the case of an esterthe rmolysis.[5,6] Any variation in symmetry of bond making and bond breaking representing a preference for a reactant-like or a productlike structure of the activated complex should produce either a reduction in magnitude of k_H/k_D (from maximum) or quantum mechanical tunnelling.[7] Such departures from transition-state symmetry can be assessed by determining the temperature dependence of k_H/k_D.[4,7]

Additionally t-butyl esters invariably show much (up to 10 kcal/mol) lower activation energies than the less reactive ethyl[8] and cyclohexyl[9] esters, for both of which k_H/k_D has been reported to have the 'maximum' value. To test these possibilities k_H/k_D has been measured for t-butyl carbamate thermolysis over a large range of temperatures using a gold coil reactor technique previously described.[10] The data are compiled in the Table and plotted in the Figure.

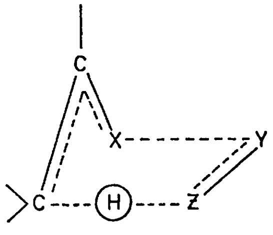
Clearly, the fact that both ethyl[5] and t-butyl esters exhibit practically (within the limits of experimental error) the maximum and nearly identical k_H/k_D values can be taken as evidence that their respective thermolytic transition states have similar structures and possess the same degree of double bond development. The magnitude of the activation energy difference which distinguishes the thermolytic eliminations of ethyl and t-butyl esters is not to be related to the factors responsible for similar magnitudes of difference observable in their solvolytic elimination reactions. That is to say, it is not to be attributed to differences in charge development or related factors that would tend to destroy the essential symmetry of the purely concerted, cyclic transition state which is characteristic of the reaction.

We have also examined another feature of the mechanistic proposals made by Tinkelenberg, Kooyman, and Louw,[1] namely the preferred planarity of the ester thermolysis transition state in which an OHC angle of 120° is envisaged. This geometry should result in a considerably smaller kinetic deuterium isotope effect than the k_H/k_D maximum predicated on a linear (coaxial) relationship of the hydrogen and the atoms between which it is transferred in the transition state.[4,5] If the gross structural relationship of the atoms involved in hydrogen transfer is capable of any great variation, as suggested by these authors,[1] it would be expected that the value of k_H/k_D would change considerably with substrate structure.[4,6]



(A)

Idealized ester thermolysis transition state



(B)

Idealized retro-ene transition state where X,Y,Z may be C,N,O,S,Si,*etc.*

Moreover, these data (Table) make evident the close parallel in structure of the ester and retro-ene thermolysis reaction transition states. The latter reaction has been shown in a growing number of cases[4,11] to exhibit a maximum k_H/k_D independently of wide variation of substituents and substrate framework atoms [see (A)] in consonance with its characterization as an orbital-symmetry, conserved pericyclic[12] process. On this basis, the ideal geometry of the ester elimination transition state may be depicted as (A) and compared with the retro-ene (B).

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